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Recombination and excitation of HeH$^+$

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Merged-beam studies have shown that the recombination of HeH$^+$ with electrons is not slow as previously believed. The initial (ground state) of the ions has been identified by examining thresholds for dissociative excitation leading to H-atom formation. The recombination of and excitation from quasimetastable excited states of HeH$^+$ have also been measured.

INTRODUCTION

The dissociative recombination of HeH$^+$ with electrons has always been assumed to have a negligible rate coefficient, since the unusual electronic structure of the molecule results in a very isolated ground state (Fig. 1). Numerous calculations[1,2] of the potential-energy curves for HeH$^+$ and HeH have failed to show any evidence for a suitable curve crossing of the ground state by a repulsive state through which the dissociative stabilization of the recombination could proceed. In addition, a recent study by Michels[1] failed to find suitable curve crossings within the excited-state manifold of HeH$^+$. It has always been presumed, therefore, that at thermal energies, e-HeH$^+$ recombination proceeds radiatively[3] with a small rate of about 2×10^{-11} cm^3 sec^{-1}.

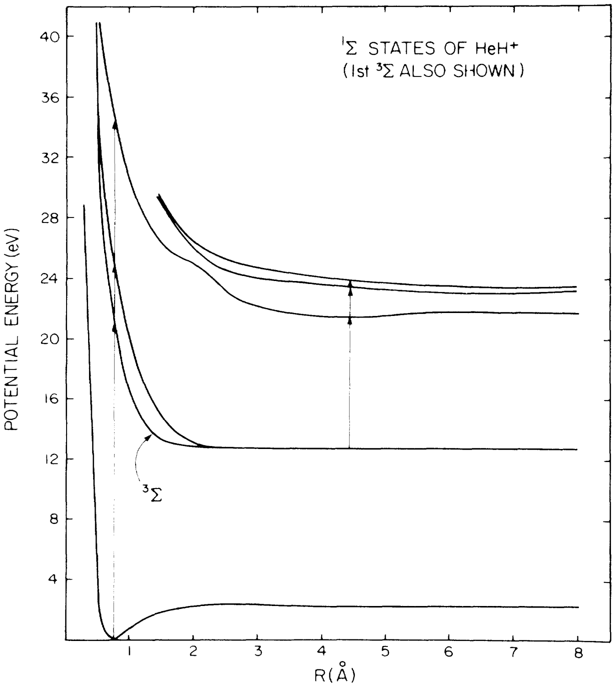

FIG. 1. Potential-energy curves for the ground and excited $^1\Sigma$ states of HeH$^+$ and the first $^3\Sigma$ state (Ref. 18). The arrows indicate the transitions seen in the electron-impact excitation results [Figs. 3(a) and (3b)].

A number of astrophysical studies have suggested that since the destruction rate of HeH$^+$ is expected to be low, the molecule may be detectable in planetary nebulas. A recent search[4] of NGC 7027, however, failed to find any evidence for HeH$^+$ emission at infrared wavelengths.

This paper describes the first detailed experimental study of HeH$^+$ recombination and reports the surprising finding that the cross section for this process is not, in fact, small at low energies. Also reported are dissociative excitation cross sections which are used to identify the initial states of the ions used in the measurements.

EXPERIMENTAL TECHNIQUE

HeH$^+$ ions are produced from a 20% He–80% H$_2$ mixture in a radio-frequency storage ion source,[5] accelerated to 400 keV, mass analyzed and merged with a variable energy electron beam. Following beam intersection, the ion beam is electrostatically analyzed to separate the primary ions from the neutrals. The ions are collected in a Faraday cup and the neutrals are detected using an energy-sensitive surface-barrier detector. Details of the apparatus has been published elsewhere.[6]

RESULTS AND DISCUSSION

The pulse height spectrum of the detector signals contains three peaks corresponding to particles with $\frac{1}{5}$, $\frac{4}{5}$, and full beam energy, respectively. The $\frac{1}{5}$ energy particles are hydrogen atoms formed from the reactions

$$e+\mathrm{HeH}^+\rightarrow\mathrm{H}+\mathrm{He}^++e\ , \tag{1}$$

$$\mathrm{HeH}^++X\rightarrow\mathrm{H}+\mathrm{He}^++X\ , \tag{2}$$

where X is a background gas molecule.

The $\frac{4}{5}$ energy particles are helium atoms from

$$e+\mathrm{HeH}^+\rightarrow\mathrm{He}+\mathrm{H}^++e\ , \tag{3}$$

$$\mathrm{HeH}^++X\rightarrow\mathrm{He}+\mathrm{H}^++X\ . \tag{4}$$

The full energy particles are HeH* molecules and He+H atom pairs formed from

$$e+\mathrm{HeH}^+\rightarrow\mathrm{He}+\mathrm{H} \tag{5a}$$

$$\rightarrow\mathrm{HeH}^*\rightarrow\mathrm{He}+\mathrm{H}+h\nu\ , \tag{5b}$$

$$\mathrm{HeH}^+ + X\rightarrow\mathrm{HeH}^* + X^+ \tag{6a}$$

$$\rightarrow\mathrm{He}+\mathrm{H}+X^+\ . \tag{6b}$$

Electron-ion reactions are distinguished from ion-background gas reactions using standard beam modulation techniques.[6] The difference in the two signal count rates yields the true electron-ion signal count rate. Signals from reactions (1), (3), and (5) are separated using single-channel analyzers. Previous experience with the storage ion source has shown that the internal energy of the ions so produced depends upon the value of the potential applied to an extraction electrode which is used to draw the ions out of the trap region. Typically, if 100 V is applied between the trap and this electrode, the resulting ion beam will contain a substantial percentage of excited ions. This is believed to be due to two effects, namely, collisional excitation due to collisions in the extraction region and diminished residence time of the ions in the trap due to the extraction field. If a very low extraction potential is applied, then a beam containing ions in low internal energy states only can be produced.

Recombination [reaction (5a) and/or reaction (5b)] and dissociative excitation [reaction (1)] cross sections were measured for two source conditions: high extraction and low extraction. The results of these measurements are shown in Figs. 2 and 3. It is most notable that both sets of conditions yield recombination cross sections that are surprisingly large. The presence of excited states in the high-extraction beam is evident from the dissociative excitation results shown in Fig. 3(a). The measured cross sections for the high-extraction case are about a factor of 5 larger than the low-extraction results. The 2-eV threshold in Fig. 3(a) and the subsequent structure can be explained in terms of transitions from the second excited, $^3\Sigma$ or $^1\Sigma$ state (Fig. 1), to upper repulsive states dissociating to He$^+$+H. These states are effectively metastable due to the very poor Franck-Condon overlap with the first excited $^3\Sigma$ or $^1\Sigma$ states. They therefore appear to be populated in the ion beam during the flight time from the ion source to the interaction region ($\sim 1\ \mu$S). In principle, it is also possible to examine transitions to states dissociating to He+H$^+$ [reaction (3)]. Unfortunately, there is such a large background noise component in this channel that the counting time required to achieve statistical accuracy is prohibitive.

The low-extraction results [Fig. 3(b)] are much cleaner. Michels[7] has calculated excitation functions for transitions between the $X\ ^1\Sigma^+$ ground state and the $a\ ^3\Sigma^+$ and $A\ ^1\Sigma^+$ states. The positions of the peaks in these functions (at 20 and 26 eV, respectively, for transitions originating from the $v=0$ level of $X\ ^1\Sigma^+$) correspond closely to those of the experimentally measured peaks shown in Fig. 3(b). The absence of peaks lower than 20 eV indicates that the ions are predominantly in their ground electronic state. No evidence for a predicted 17.4-eV

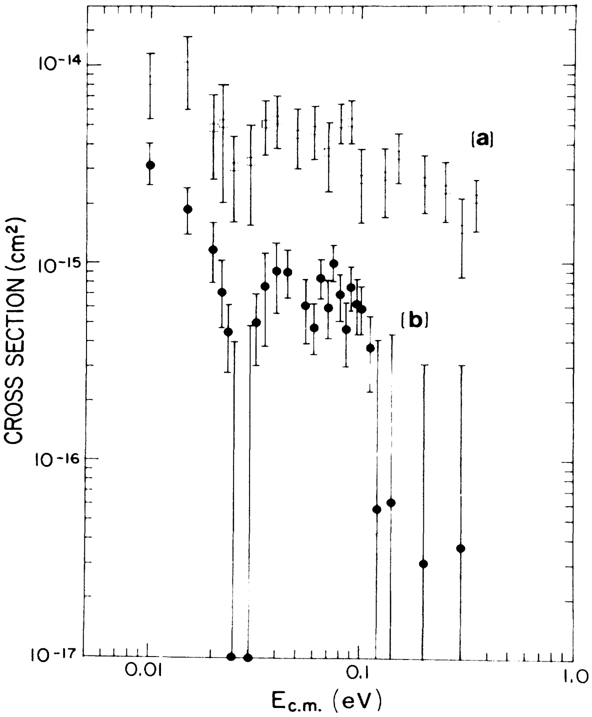

FIG. 2. Measured dissociative recombination cross sections for HeH$^+$ ions prepared under (a) high-extraction and (b) low-extraction conditions.

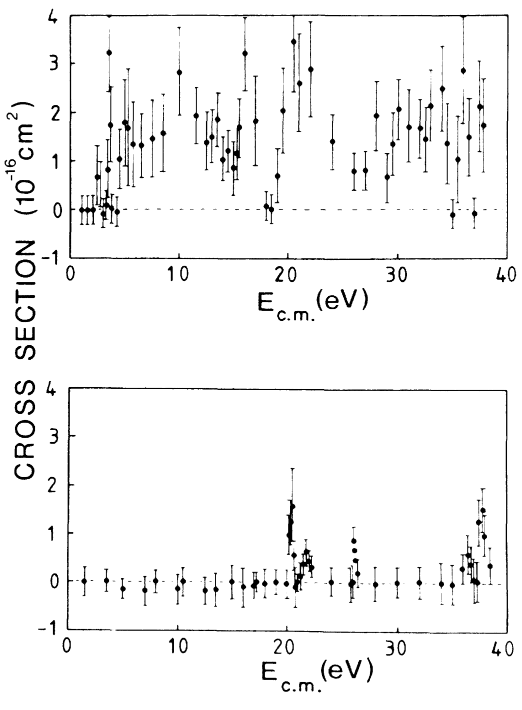

FIG. 3. Measured dissociative excitation cross sections for HeH$^+$ ions prepared under (a) high-extraction and (b) low-extraction conditions.

peak arising from the excitation from the $v=1$ level of the ground state of HeH^+ to the upper states was found, suggesting that the ions are predominantly in the $v=0$ level.

The fact that the peaks seen in the measurement are so narrow is not well explained at this time. Indeed, the peak at 26 eV, corresponding to a transition from the ground state to the first excited $^1\Sigma$ state, was not initially seen in the experiment. Following communication of the calculated results, a search was made and the structure was subsequently found. It had been overlooked in the original measurement due to its narrowness. One possibility is that the upper repulsive states are not as steep in the Franck-Condon region as indicated in Fig. 1. Another is that the sharp structures are evidence of doubly excited resonant neutral states lying just below the excited ion states into which the incoming electron is temporarily captured. Such a process is reminiscent of dielectronic recombination[8] in atomic ions, except that in this case the resonant states are rapidly predissociated before they can be radiatively stabilized. Similar structures have been seen in measurements of the electron-impact dissociative excitation of N_2^+ (Ref. 9) and H_3^+ (Ref. 10) ions, suggesting that this phenomena is rather common. Unfortunately, such doubly excited states are difficult to model and theoretical information about them is not currently available. It is to be hoped that these results will stimulate such calculations.

If one accepts the resonance explanation for the narrowness of the peaks, one might wonder why the direct excitation from the ground state to the excited ion state is not evident in the results. It could be that this is a situation similar to that for the ionization of molecular hydrogen where the threshold region is dominated by transitions to autoionizing vibrationally and rotationally excited Rydberg states, the direct ionization being much weaker.[11] Clearly, much more work is required before a satisfying explanation can be given for this phenomenon.

With regard to the recombination of HeH^+, direct capture appears to be ruled out due to the absence of an intersection with a suitable neutral state. It is possible, however, for the recombination to proceed via the indirect mechanism in which the electron is captured into a vibrationally excited Rydberg state of the neutral molecule. Such a state might subsequently be stabilized radiatively. Again, this is a process akin to dielectronic recombination. Alternatively, it is known that several of the HeH^* states are strongly predissociated[12] and this might offer a rapid decay path. Interestingly, such predissociation is not seen for the Rydberg states of ^3HeD and at a later date it is our intention to examine the recombination of $^3HeD^+$. If there is a strong isotope effect this would lend support to the hypothesis that the recombination proceeds via Rydberg-state capture.

A striking feature in the low-extraction results is the very deep resonance which occurs in the (20–30)-meV region. The step drop-off above 0.1 eV may also be due to resonances. Such structure is caused by interactions involving autoionizing, vibrationally excited Rydberg states of the neutral molecule.[13] The ability to see such resonances is due to the high-energy resolution of the merged-beam technique. In experiments on H_2^+ recombination, resonances with a width of less than 20 meV have been seen.[14] The large resonance centered at 0.27 eV also appears in the high-extraction results, but it is partially obscured due to contributions to the recombination cross section from excited ions.

Adams and Smith[15] (AS) have also examined the recombination of HeH^+ using a flowing afterglow Langmuir probe (FALP) technique. In this experiment, the decay of ions in an afterglow plasma is studied as a function of time in order to determine the recombination-rate coefficient. It was found in this experiment that the measured decay rates for HeH^+, He^+, and H_3^+ were indistinguishable and AS proposed that the HeH^+ and H_3^+ ions would therefore have the same rate coefficient as that calculated[3] for the radiative recombination of He^+, i.e., 2×10^{-11} cm^3 sec^{-1} at 300 K. The problem with this statement is that the sensitivity of the FALP technique is insufficient to make such a comparison of decay rates to that level of accuracy. Measurements of the decay rate of ions are limited by the diffusion loss rate to the walls of the apparatus,[16] which is of the order of 2×10^{-8} cm^3 sec^{-1}. The electron density in the afterglow is $\sim10^{10}$ cm^{-3}, and at 300 K, collisional radiative recombination[17] of ions would be expected to proceed at a rate of about 4×10^{-10} cm^3 sec^{-1}. This is below the level of accuracy of the technique and so this process cannot be distinguished from radiative recombination. If a binary mechanism exists that would allow a molecular ion to recombine faster than the radiative rate typical of an atomic ion, and yet slower than the typical diffusion loss rate, this could not be identified with the FALP apparatus.

Derivation of a rate coefficient from the results shown in Fig. 2 is not easy because of the resonant structures, but one can estimate the value at 300 K to be about 1×10^{-8} cm^3 sec^{-1} assuming a linear dependence of the cross section, over the measured range. In fact, the presence of the deep resonance in the region between 0.02 and 0.04 eV (corresponding to a temperature range from 220 to 440 K) would lead to a lowering of the rate coefficient below this value in this region.

SUMMARY

The results presented here show that, contrary to previous belief, the recombination rate for HeH^+ is not negligible. Given the absence of a suitable curve crossing, direct recombination appears to be ruled out and so the process must proceed via the indirect mechanism, i.e., via electron capture into an autoionizing Rydberg state. This system is therefore a unique test bed for studies of molecular ion recombination where the indirect mechanism dominates. Future experimental and theoretical studies of this phenomenon are planned.[7]

ACKNOWLEDGMENTS

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[1] H. H. Michels, in *Dissociative Recombination: Theory, Experiment and Applications,* edited by J. B. A. Mitchell and S. L Guberman (World Scientific, Singapore, 1989), p. 97, and references therein.

[2] I. D. Petsalakis, G. Theodorakopoulos, and R. J. Buenker, Phys. Rev. A **38**, 4004 (1988).

[3] D. R. Bates and A. Dalgarno, in *Atomic and Molecular Processes,* edited by D. R. Bates (Academic, New York, 1962), p. 245.

[4] J. M. Moorhead, R. P. Lowe, J. P. Maillard, W. H. Wehlau, and P. F. Bernath, Astrophys. J. **326**, 899 (1988).

[5] E. Teloy and D. Gerlich, Chem. Phys. **4**, 417 (1974).

[6] D. Auerbach, R. Cacak, R. Caudano, T. D. Gaily, C. J. Keyser, J. W. McGowan, J. B. A. Mitchell, and S. F. J. Wilk, J. Phys. B **10**, 3797 (1977).

[7] H. H. Michels (private communication).

[8] Y. Hahn, Adv. At. Mol. Phys. **21**, 124 (1985).

[9] C. Noren, F. B. Yousif, and J. B. A. Mitchell, J. Chem. Soc. Faraday Trans. 2 (to be published).

[10] F. B. Yousif, K. Vanderdonk, and J. B. A. Mitchell (unpublished).

[11] W. B. Peatman, J. Chem. Phys. **64**, 4368 (1975), and references therein.

[12] R. L. Brooks, J. L. Hunt, and D. J. Miller, Phys. Rev. Lett. **58**, 199 (1987), and references therein.

[13] A. Giusti, J. N. Bardsley, and C. Derkits, Phys. Rev. A **28**, 682 (1983).

[14] H. Hus, F. B. Yousif, C. Noren, A. Sen, and J. B. A. Michell, Phys. Rev. Lett. **60**, 1006 (1988).

[15] N. G. Adams and D. Smith, in Ref. 1, p. 124.

[16] N. G. Adams, D. Smith, and E. Alge, J. Chem. Phys. **81**, 1778 (1984).

[17] J. Stevefelt, J. Boulmer, and J. F. Delpech, Phys. Rev. A **12**, 1246 (1975).

[18] T. A. Green, H. H. Michels, J. C. Browne, and J. A. Madsen, J. Chem. Phys. **61**, 5186 (1974); T. A. Green, H. H. Michels, and J. C. Browne, *ibid.* **69**, 101 (1978).